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REMOVAL OF ACUTE TOXICITY FROM A SIMULATED KRAFT MILL EFFLUENT IN AERATED LAGOONS

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INTRODUCTION

Aerated lagoons are a common and effective means of removing BOD from the effluent of pulp and paper mills. Gehm (1) has enumerated several reasons for the selection of aerated lagoons for secondary treatment.

Secondary treatment is especially needed for mills located on streams which undergo seasonal periods of low flow and high water temperatures. Many such mills are located in the southern United States, where the ready availability of land makes aerated lagoons an economically attractive treatment method.

Aerated lagoons are more reliable than physical or chemical methods of effluent treatment. They are not as subject to mechanical breakdowns and generally handle shock loads without serious upset. And finally, capital and operating costs are lower than that of physical or chemical treatment systems.

It seems likely that in the near future, environmental regulations on both the state and federal levels will be promulgated to incorporate standards pertaining to the allowable toxicity of discharges into receiving waters. This possibility has prompted several studies of the removal of toxicity in secondary treatment plants.

EXPERIMENTAL METHODS

Three bench-scale aerated lagoons were constructed with hydraulic detention times of 4, 12, and 24 days. A simulated kraft pulp mill effluent was fed to the lagoons, and effluents were collected for study. The parameters measured were total and soluble BOD, total and soluble COD, mixed liquor total and volatile suspended solids, effluent total and volatile suspended solids, and pH. Resin and fatty acids were extracted from feed and effluent samples and analyzed by gas chromatography.

Acute bioassays were performed on both simulated whole mill effluent and filtered (0.45 membrane filter) effluent. The early instars and adults of *Daphnia magna*, and the adults of *Daphnia schødleri* were assayed. Acute toxicity to the fathead minnow (*Pimephales promelas*) was measured by the residual oxygen assay method. Algal assays (9) were performed on the effluent, to determine its effect upon the test alga, *Selenastrum capricornutum*.

Black Liquor Generation

The kraft black liquor for this study was obtained by pulping jack pine chips (*Pinus banksiana*). The chips were made from jack pine logs chipped in a laboratory chipper to a size of 7/8" by 1/2". The chips were stored at 0°C for the duration of the project to retard aging of the wood. The composition of the pulping liquor was 40.6 g/l Na_2S and 204.2 g/l NaOH, or 17.9% active alkali, and 28.1% sulfidity. Pulping was carried out in laboratory pressure vessels which were rotated in a heated oil bath.

A pulping sequence was performed weekly to minimize problems with black liquor decomposition. The liquor to wood ratio was 4:1. The chips were heated from 70° to 173° in 90 minutes, and cooking was continued until an H-factor (2) of 1000 was reached. This pulping sequence is typical of a northern kraft mill producing linerboard.

When the target H-factor was reached, the chips were removed from the oil bath and transferred to a cooling chamber. After cooling, the cooking liquor was decanted. The pulp was then washed and decanted again. The decanted cooking liquor and pulp washings were combined and comprised the black liquor.

Feed Preparation

Approximately 70 liters of feed were prepared on a weekly basis. Each batch consisted of 200 ml of filtered black liquor diluted to ten liters with cold tap water. Sufficient nitrogen and phosphorus were added to the black liquor to give a BOD:N:P ratio of 100:20:1. This dilution was chosen to simulate a kraft mill effluent with a BOD_5 of approximately 150 mg/l, based upon preliminary BOD_5 determinations performed upon the kraft liquor. The 10 liter batch of feed was then neutralized to pH 7.1 $\pm$ 0.1 with HCl.

Lagoon Operation

The lagoons were fed at a rate of 3 liters per day. The No. 1 lagoon had a nominal hydraulic retention time of 4 days; the No. 2 lagoon, 12 days; and the No. 3 lagoon, 24 days.

Air was supplied to the lagoons by compressed air after removal of entrained oil and water. The feed for the lagoons was stored at 4°C in a 5-gallon carboy.

Dow-Corning Antifoam-A Emulsion was added daily (1-3 drops) to each lagoon and the foam was scraped off the freeboard and mixed back into the lagoon.

The lagoon feed tank was refilled daily from the cold storage tank. A 200 ml sample of mixed liquor was collected daily from each lagoon. The effluent was filtered (glass wool) into a 2 liter separatory funnel, where it was allowed to settle for thirty minutes. The filtering and settling simulated the operation of a secondary settling pond. After settling, the bottom portion was drained off. The remaining sample was placed in a stoppered 2 liter Erlenmeyer flask until final testing.

Testing of Effluent

Analytical tests were performed according to Standard Methods (3).

Resin and fatty acids were determined according to the gas chromatographic method of Easty, et al. (4).

Bioassay Procedures

Culture and Collection of *Daphnia* sp.

The *Daphnia magna* culture was started from a single adult female obtained from a laboratory stock. Parthenogenic female offspring were periodically harvested for test specimens. The *Daphnia schødleri* culture was started from a single adult female obtained from wild stock from the Fox River at Menasha, Wisconsin.

Bioassays

The Daphnia bioassays were carried out in 250 ml Pyrex beakers. Tests were performed on simulated whole mill influent, whole mill effluent and the filtered effluent. The concentrations of effluent used for bioassays testing were 100%, 75%, 50%, 21% and 0% (Control). Distilled, deionized water was used for dilution. Each test beaker contained 100 mls of effluent.

Two sets of five animals each were placed in separate beakers for each species (adult or immature) and effluent concentration. The animals were taken randomly from a holding beaker with a large bore pipet and counted into separate, small glass dishes. Excess water was removed with a pipet and the dishes submerged in the test solutions to release the *Daphnia*.

Immobilization was used as the criterion for determination of EC_{50} values. Immobilization was defined as the inability of the animal to propel itself even after gentle prodding with a pipet. The number of non-immobilized animals were counted and recorded at 24 hour intervals. Temperature and pH were recorded at the beginning of the test and at 24 hour intervals thereafter. Each assay lasted 96 hours.

Fathead minnows (*Pimephales promelas*) were used in the residual oxygen assay (sealed bottle test) as described by Ballard and Oliff (6) and used by Vigers and Maynard (7) and McLeay (8). Fish loadings of 4-6 g/l in standard 300 ml BOD bottles were used at ambient temperatures varying between 20 and 22°C.

The algal assay methodology utilized was that recommended by EPA (9). The target organism was the green planktonic algae, *Selanastrum capricornutum*. The test effluents were centrifuged to remove suspended solids.

RESULTS AND DISCUSSION

The results of the *Daphnia* bioassays are given in Table I. The influent was toxic to *D. magna* early instars and *D. magna* adults in both the 48 hour and 96 hour bioassays. However, *D. schødleri* bioassays indicated no toxicity after either 48 hours or 96 hours. The greater resistance of *D. schødleri* will be further discussed below.

The 48 hour Daphnia bioassays indicated a complete removal of acute toxicity from the simulated whole mill effluents at all three detention times. Removal of toxicity from the filtered effluent was less than complete (48 hour Daphnia assays) in the 4 day and 12 day lagoons. The 24 day lagoon did remove the acute toxicity for the filtered effluent as indicated by the 48 hour Daphnia bioassays.

The difference in results between filtered and whole effluent (Table I) may have been due to the presence of biosolids which have been demonstrated as a food source for Daphnia (12). The lack of solids in the filtered effluent may have contributed to stressing the exposed Daphnia which caused greater susceptability to mill effluents, or resulted in starvation of the test subjects.

The results of the 96 hour bioassays are similar to those of the 48 hour tests. The 4 day and 24 day lagoons removed all the acute toxicity from the simulated whole mill effluent. The results for the 12 day lagoon indicate that the effluent's EC_{50} is less than 21%. This is believed to be a spurious result, the cause of which is unknown. Removal of toxicity in the filtered effluent was less complete. Again, this may be the result of starvation which weakened the *Daphnia* in the filtered effluent bioassays.

Substantial differences exist in the bioassay results between *D. magna* and *D. schødleri*. This can best be illustrated by the influent test results. In the 48 hour tests, the EC_{50} values of *D. magna* early instars and adults were 69% and 59%, respectively; the value of *D. schødleri* adults was greater than 100%, indicating

that *D. schødleri* are more resistant to the toxic effects of the simulated mill effluent than are *D. magna*. The 96 hour EC_{50} values follow the same pattern.

The average values of COD, BOD_5, and suspended solids for the influent and effluents are shown in Table II. The three lagoons did not perform well in removing total COD. It would appear that the majority of the remaining COD in the effluents is in the solids fraction: all three lagoons removed a majority of soluble COD. The residual soluble COD is probably composed mostly of non-biodegradable lignin compounds. No correlation was found between the COD and acute toxicity.

BOD appears to correlate rather well with resin and fatty acid concentrations in the test effluents. There is, however, insufficient data to conclude that BOD is a good predictor of resin and fatty acid concentrations.

The relationship between hydraulic retention time and resin and fatty acid removal is shown in Figures 1 and 2. Dehydroabietic acid was quickly removed, while linoleic and abietic acids were removed more slowly. This may be significant, in that Dumouchel (10) found linoleic acid to be more toxic than dehydroabietic acid.

Rates of resin and fatty acid degradation are shown in Table III. Neither dehydroabietic acid nor pimaric acid was found to be degraded as quickly as reported previously (11). However, that study was performed on batch reactors, not continuous-feed lagoons. Thus, the results in Table III may indicate that excess removal capacity exists in the aerated lagoons.

The results of the residual oxygen assay are presented in Table IV. These data indicate no apparent acute toxicity for the treated effluents from all three test lagoons.

The response of *Selanastrum capricornutum* to the effluents was variable. At low concentrations, the effluents appeared to be mildly stimulatory. At the higher concentrations, i.e., above 10%v effluent, the results were obscured as a result of substantial bacterial growth within the test flasks. Microscopic examination of the test flasks on the final day of the test revealed that biomass in the higher concentrations was almost entirely bacterial. The results of these tests are presented in Table V.

CONCLUSIONS

1. All of the lagoons were successful in removing acute toxicity in the simulated whole mill effluent. The tests indicated that some toxicity to *Daphnia* remained in the filtered effluent. These results were ascribed to lack of biosolids in the filtered effluent.

2. *D. schødleri* were found to be more resistant to the toxic effects of the effluents than *D. magna*.

3. BOD and COD cannot be relied upon as predictors of toxicity, although they may be related to resin and fatty acid content.

4. Dehydroabietic acid was the most easily degraded resin acid.

5. There is good correlation between hydraulic retention time and effluent concentration of resin and fatty acids.

Table I. Results of 48 hour and 96 hour *Daphnia* bioassays

		48 hour EC_{50} values			
		Influent	4 day Lagoon	12 day Lagoon	24 day Lagoon
D. magna	whole	69%	>100%	>100%	>100%
Early instars	soluble	69%	61%	100%	>100%
D. magna	whole	59%	>100%	>100%	>100%
Adults	soluble	59%	84%	92%	>100%
D. schødleri	whole	>100%	>100%	>100%	>100%
Adults	soluble	>100%	38%	>100%	>100%

		96 hour EC_{50} values			
		Influent	4 day Lagoon	12 day Lagoon	24 day Lagoon
D. magna	whole	69%	>100%	<21%	>100%
Early instars	soluble	69%	50%	79%	>100%
D. magna	whole	50%	>100%	<21%	>100%
Adults	soluble	50%	36%	38%	>100%
D. schødleri	whole	>100%	>100%	<21%	>100%
Adults	soluble	>100%	21%	>100%	>100%

Table II. COD, BOD , and Suspended Solids Values.

	Influent	4 days	12 days	24 days
Effluent total COD, mg/l	560	405	415	385
% removal		27%	25%	31%
Effluent soluble COD, mg/l		230	210	160
% removal		58%	62%	71%
Effluent total BOD, mg/l	145	40	35	20
% removal		71%	74%	85%
Effluent soluble BOD, mg/l		12	11	8
% removal		92%	92%	94%
Mixed liquor SS, mg/l		200	220	215
Effluent SS, mg/l		40	8	15

Table III. Rate of degradation of resin and fatty acids (Based on an average MLSS of 210 mg/l)

Acid	Degradation Rate, µg/mg biosolids/day
Oleic	.033
Linoleic	.005
Pimaric	.014
Isopimaric	.042
Abietic	.005
Dehydroabietic	.052
Total	.118

Table IV. Residual Oxygen Assay

Effluent Conc. (%)	Lagoon Detention Time (days)		
	4	12	24
	Residual Oxygen (mg/l)		
100	.4	.4	.6
75	.4	.4	.6
50	.4	.4	.5
37	.5	.3	.5
21	.6	.4	.5
15	.7	.4	.6
10	.6	.6	.6
4	.7	.6	.6
0	1.0	.6	.8

Table V. Algal Bioassay Results

Concentration (%v)	Lagoon Detention Time (days)		
	4	12	24
	mg/l biomass		
Control	160	160	160
4	323	305	348
10	180	B*	175
21	B	B	B
37	B	B	B
50	B	B	B
75	B	B	B
100	B	B	B

*B≡ Culture predominantly bacteria

Figure 1. Effluent total resin and fatty acids vs. hydraulic detention time.

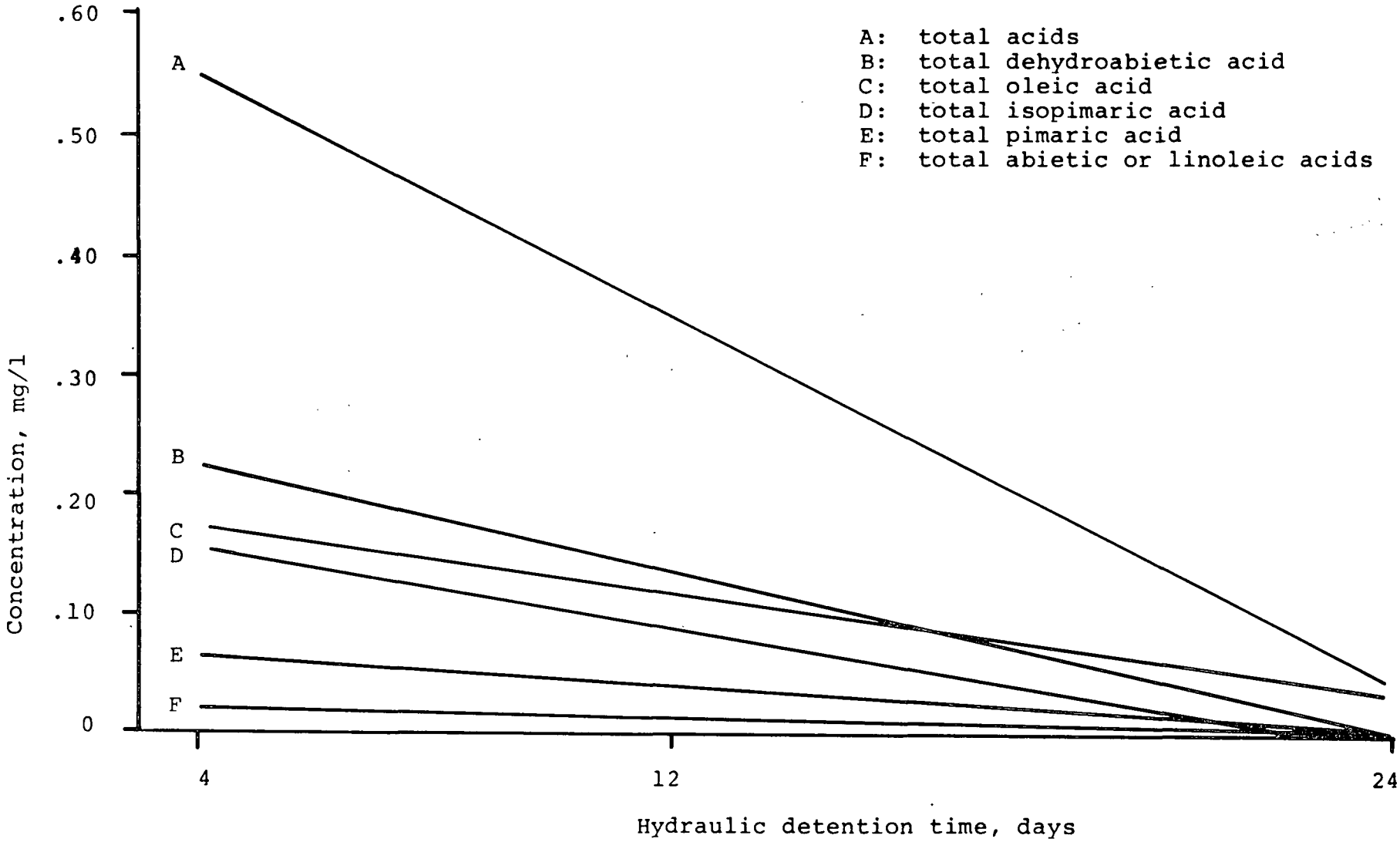
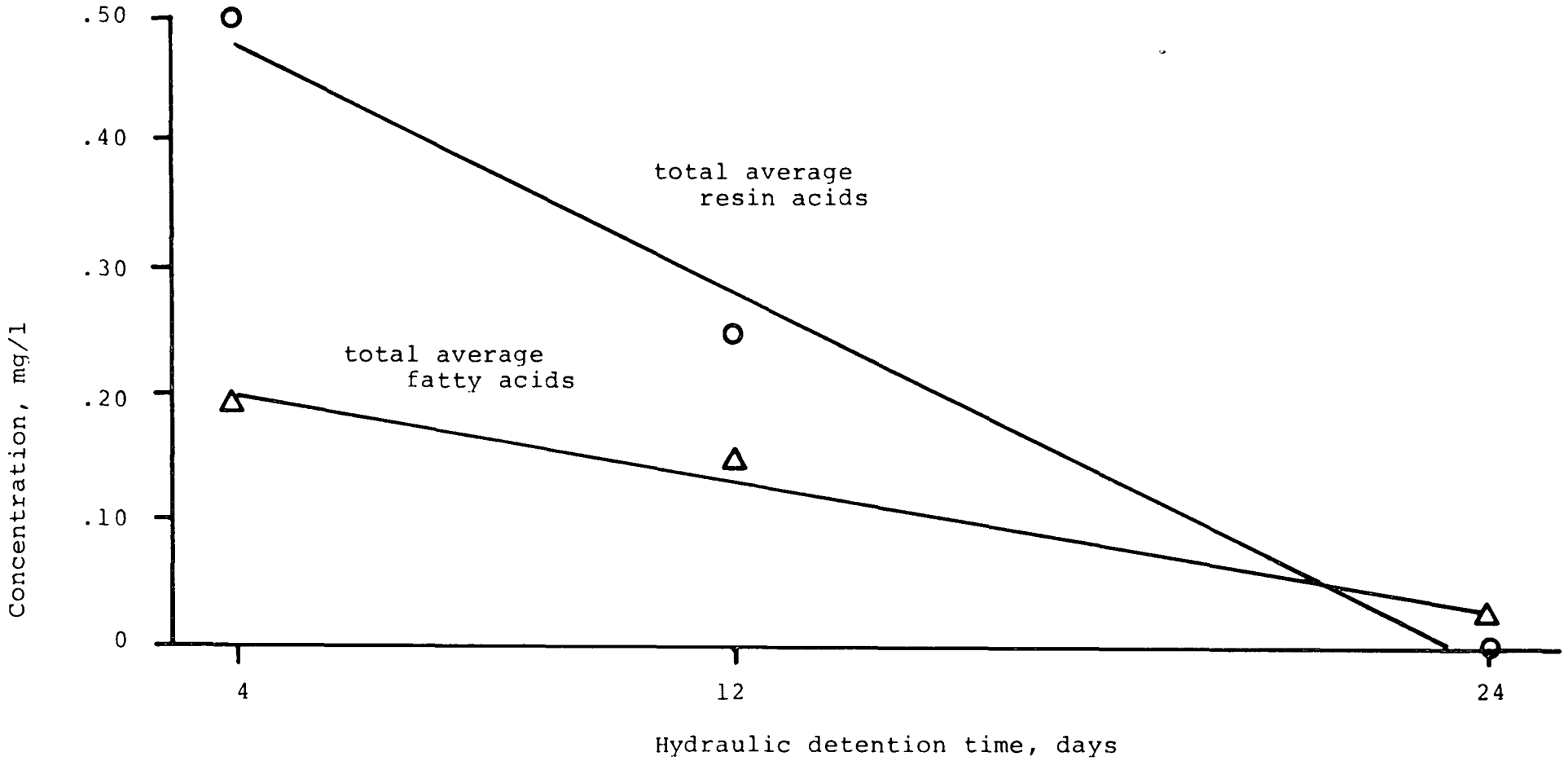


Figure 2. Effluent total average resin and fatty acids vs. hydraulic detention time



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